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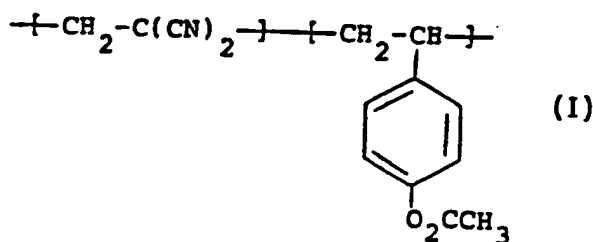
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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification 5 : C08F 222/34, B29C 35/02 B06B 1/02, G11C 13/02</p>	<p>A1</p>	<p>(11) International Publication Number: WO 91/13922 (43) International Publication Date: 19 September 1991 (19.09.91)</p>
<p>(21) International Application Number: PCT/US90/06751 (22) International Filing Date: 16 November 1990 (16.11.90) (30) Priority data: 491,138 9 March 1990 (09.03.90) US (71) Applicant: HOECHST CELANESE CORPORATION [US/US]; Patent Department, 86 Morris Avenue, Summit, NJ 07901 (US). (72) Inventors: EAST, Anthony, J. ; 62 Niles Avenue, Madison, NJ 07940 (US). CONCIATORI, Anthony, B. ; 27 Orchard Road, Chatham, NJ 07928 (US). (74) Agents: WINTER, Richard, C.; PCT International, Inc., c/o Hoechst Celanese Corporation, Patent Department, 86 Morris Avenue, Summit, NJ 07901 (US) et al.</p>		<p>(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent). Published With international search report.</p>

(54) Title: VINYLIDENE CYANIDE ALTERNATING COPOLYMERS



(57) Abstract

In one embodiment this invention provides vinylidene copolymer with alternating monomeric units as illustrated by structure (I). An invention vinylidene copolymer in the form of an electret film exhibits a high level of longitudinal piezoelectric effect, and has excellent processability and thermal stability properties.

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VINYLLIDENE CYANIDE ALTERNATING COPOLYMERSBACKGROUND OF THE INVENTION

Electrets of organic materials are produced by applying a DC voltage to stretched films of polymers such as polyvinyl fluoride, polyvinylidene fluoride, polyvinyl chloride, polyvinylidene fluoride, polyvinyl chloride, polyacrylonitrile, polycarbonate or nylon 11, while maintaining the films at high temperature and then cooling. These films exhibit piezoelectric and pyroelectric properties.

Polymeric electret elements are useful in electro-acoustic conversion devices, electro-mechanical conversion devices, pressure-sensitive elements, bimorph elements, microwave-detention devices, image-recording light-sensitive elements, and the like.

Publications of background interest with respect to the present invention include United States Patent Numbers 2,615,868 and 4,591,465, which describe copolymers of vinylidene cyanide.

There is continuing interest in the development of novel polymeric materials which exhibit improved piezoelectric and pyroelectric properties, and superior moldability and thermal stability.

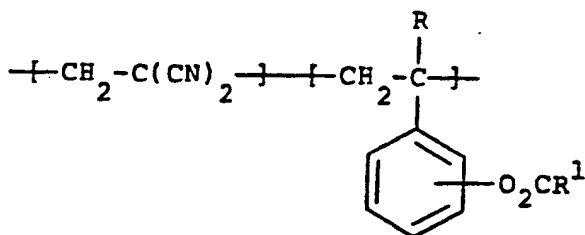
Accordingly, it is an object of this invention to provide novel copolymers which exhibit piezoelectric and pyroelectric properties.

It is further object of this invention to provide polymeric electret films which exhibit a high longitudinal piezoelectric effect.

Other objects and advantages of the present invention shall become apparent from the accompanying description and examples.

DESCRIPTION OF THE INVENTION

One or more objects of the present invention are accomplished by the provision of a copolymer which is characterized by alternating monomeric units
 5 corresponding to the formula:



where R is hydrogen, halogen or a C₁-C₄ alkyl substituent; and R¹ is hydrogen or a C₁-C₈ hydrocarbyl substituent.

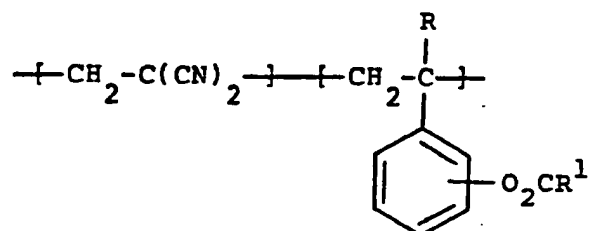
Illustrative of R and R¹ substituents, respectively,
 10 are chloro, bromo, methyl, ethyl, propyl, n-butyl, hexyl, octyl, cyclohexyl, phenyl, and the like.

A present invention vinylidene cyanide copolymer typically has a weight average molecular weight in the range between about 5000-200,000. The copolymers
 15 generally are soluble in organic solvents such as dimethylformamide, acetone or butyrolactone, and insoluble in benzene or toluene.

The polymerization can be conducted by dissolving vinylidene cyanide and the styrene monomer (1:1) in an
 20 aromatic solvent such as toluene, and heating the reaction mixture at a temperature between about 30°-100°C

for a period of about 0.5-2 hours. The copolymer separates as a white powder during the polymerization reaction. The rate of polymerization can be accelerated by the addition of about 0.01-1% by weight, based on
 5 monomer weight, of a catalyst such as a peroxygen compound as exemplified by benzoyl peroxide, cumene hydroperoxide, tertiary-butyl hydroperoxide, and the like.

In another embodiment the invention provides an
 10 electret film of a thermoplastic copolymer which is characterized by alternating monomeric units corresponding to the formula:



where R is hydrogen, halogen or a C₁-C₄ alkyl substituent;
 15 and R¹ is hydrogen or C₁-C₄ hydrocarbyl substituent;
 wherein the film has an external electric field-induced net dipolar orientation of polymer molecules, and the film exhibits piezoelectric properties.

The electret film exhibits an enhanced level of
 20 piezoelectric and pyroelectric response if the film copolymeric matrix additionally has a crystallographic

molecular orientation in the film plane which has been induced by longitudinal uniaxial mechanical stretching, or by longitudinal and transverse biaxial mechanical stretching, prior to the electric field polarization procedure. Techniques for molecular orientation in polymeric electret films by stretching or by an electric field are described in publications such as U.S. Patent Number 4,302,408 and U.S. Patent Number 4,591,465.

A vinylidene cyanide copolymer film of the present invention can be formed by press molding, calender molding or solvent casting. The film can be stretched 2-6 lengths by mechanical monoaxial or biaxial stretching with a calendar rolling or stretching apparatus.

Poling of a polymeric electret film can be accomplished by heating the film at a temperature which is lower than the glass transition temperature, applying a DC electric field (100-1500 kv/cm) to the film by electrodes for a period of about 0.1-2 hours, and then cooling the film while maintaining the external field poling bias.

A present invention vinylidene cyanide copolymer has excellent processability and thermal stability properties, and can be formed into an electret film which is amenable to stretching and electric field modes of molecular orientation, and which exhibits a high piezoelectric modulus.

As a further advantage of a present invention vinylidene cyanide copolymer, the acyloxy substituent on the styrene monomeric structure can be modified or replaced with a group which exhibits a desirable property, such as nonlinear optical susceptibility.

The following examples are further illustrative of the present invention. The components and specific ingredients are presented as being typical, and various

5

modifications can be derived in view of the foregoing disclosure within the scope of the invention.

EXAMPLE I

Preparation of an alternating copolymer of vinylidene cyanide and 4-acetoxystyrene in accordance with the present invention.

5 All glassware was acid-washed, dried and treated with trimethylsilyl chloride in toluene.

Vinylidene cyanide was prepared by the pyrolysis of 1-acetoxy-1, 1-dicyanoethane at 650°C in a vertical quartz tube packed with quartz fragments. The crude
10 pyrolysis product was collected in a cold trap at -60°C, and redistilled under reduced pressure into a receiver containing a trace of methanesulfonic acid to inhibit polymerization.

The vinylidene cyanide content of the pyrolyzate was
15 estimated by allowing a sample to homopolymerize in water, and recovering the polymer. It was determined that a 21 g quantity of pyrolyzate was equivalent to 10 g of pure vinylidene cyanide.

A reaction flask fitted with a stirrer, reflux
20 condenser and pressure-equalizing tap-funnel was heated to 70°C. The reactor was charged with a mixture of 21 g of redistilled pyrolyzate (10 g), 10 ml of glacial acetic acid and 1.0 ml of a 4% w/v solution dibenzoyl peroxide catalyst in dry chlorobenzene. 4-Acetoxystyrene (20 g)
25 was added in portions to the reaction flask contents at 70°C. After a polymerization period of about 1.5 hours, vinyl acetate was added to react with any residual vinylidene cyanide.

The excess vinyl acetate was decanted and the
30 resultant white precipitate was recovered and dissolved in acetone. The acetone solution was added to methanol to reprecipitate the polymer (24 g).

The infra-red spectrum showed a weak cyanide band at 2280 cm⁻¹, which is characteristic of polymers with a

gem-dicyano structure. Nuclear Magnetic Resonance (proton and Carbon-13) indicated that the polymer was a regularly alternating copolymer of vinylidene cyanide and 4-acetoxystyrene. Differential Scanning Colorimetry
5 indicated that the polymer was amorphous, with a strong glass transition temperature inflexion at about 182°C. The inherent viscosity as measured in a 0.5% w/v solution in gamma-butyrolacetone was 1.22 at 25°C.

Anal. calc. for alternating copolymer:

10 C, 69.53; H, 4.95; N, 11.89

Found:

C, 70.00; H, 5.00; N, 11.67

Following the procedures described above, copolymers of vinylidene cyanide are produced with each of the
15 following comonomers:

alpha-methyl-3-acetoxystyrene;

alpha-chloro-2-propanoyloxystyrene;

4-butanoyloxystyrene; and

4-benzoyloxystyrene.

EXAMPLE II

This Example illustrates the dielectric properties of a vinylidene cyanide/4-acetoxystyrene copolymer in accordance with the present invention.

5 A butyrolactone solution of a vinylidene cyanide/4-acetoxystyrene copolymer was spin-coated onto conductive indium-tin oxide glass slides, and a gold electrode was vacuum deposited on the surface of each copolymer-coated glass slide.

10 Each glass slide was heated to 170°C, and poled by applying a gradually increasing DC electric field. The maximum electric-field was equivalent to about 85 volts/micron. Above this voltage level dielectric breakdown occurred.

15 Each poled film was measured for its pyroelectric coefficient "p" was measured by a method substantially as described in J. Phys. E., 5,787 (1972) by Hartley et al; and the opto-electronic coefficient "r" was measured by a laser reflectance technique as described in Proc. S.P.I.E., 1147, 222 (1989) by Haas et al. The measured values were compared with those for a known vinylidene cyanide/vinyl acetate type of copolymer. The comparative data are summarized in Table I.

25 The relative permittivity and dielectric loss properties of the invention vinylidene cyanide/4-acetoxystyrene copolymer were measured and compared with the vinylidene cyanide/vinyl acetate copolymer. The comparative data are summarized in Tables II-III.

TABLE I

FILM NUMBER	LOADING LEVEL %	THICKNESS MICRONS	FIELD V/ μ m	T °C	"r" "p" pm/V
<hr/>					
5	<u>Vinylidene cyanide/vinyl acetate copolymer</u>				
1.	8	8.5	100	167	5.5 -
2.	8	8.1	100	167	10.6 1.00
3.	8	8.3	100	167	9.2 0.97
 <u>Vinylidene cyanide/4-acetoxystyrene copolymer</u>					
10	4.	10	4.26	80	170 3.5 -
	5.	10	6.03	65	170 4.4 0.47
	6.	14	5.7	85	163 3.5 -
	7.	14	3.75	80	167 3.6 -

10

TABLE IIRelative Permittivity (epsilon)

5	FREQUENCY kHz	COPOLYMER(1)	COPOLYMER(2)
	0.1	4.34	4.86
	1.0	4.15	4.76
	10.0	3.97	4.68
	100.0	3.80	4.58

10 (1) Vinylidene cyanide/vinyl acetate

(2) Vinylidene cyanide/4-acetoxystyrene

TABLE IIIDielectric Loss (tan delta)

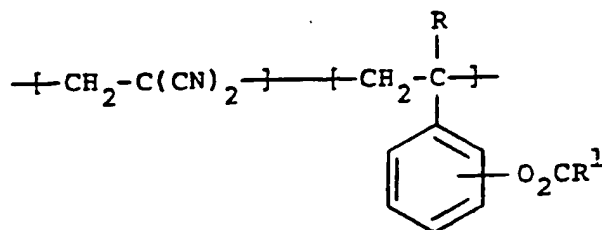
. 5	FREQUENCY	COPOLYMER(1)	COPOLYMER(2)
	kH _z		
10	0.1	4.10	1.30
	1.0	3.05	1.27
	10.0	3.17	1.66
	40.0	3.37	3.40
	100.0	4.90	5.80

(1) Vinylidene cyanide/vinyl acetate

(2) Vinylidene cyanide/4-acetoxystyrene

WHAT IS CLAIMED IS:

1. A copolymer which is characterized by alternating monomeric units corresponding to the formula:



where R is hydrogen, halogen or a C₁-C₄ alkyl substituent;
 5 and R¹ is hydrogen or a C₁-C₈ hydrocarbyl substituent.

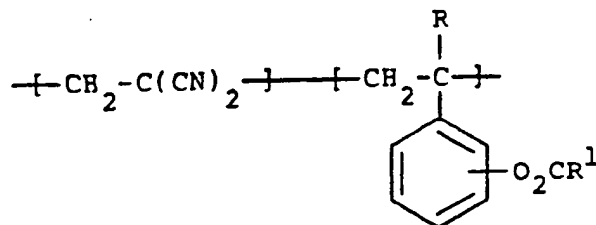
2. A copolymer in accordance with claim 1 wherein R is hydrogen or methyl.

3. A copolymer in accordance with claim 1 wherein R¹ is methyl or phenyl.

10 4. A copolymer in accordance with claim 1 wherein the copolymer has a weight average molecular weight in the range between about 5000-200,000.

15 5. An electret film of a thermoplastic copolymer which is characterized by alternating monomers units corresponding to the formula:

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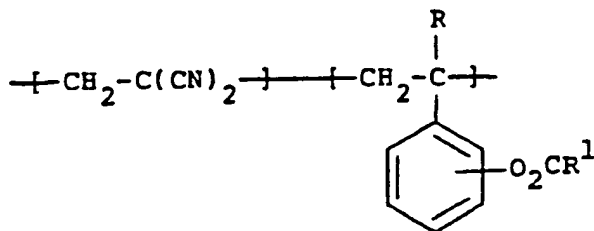
where R is hydrogen, halogen or a C₁-C₄ alkyl substituent;
 and R¹ is hydrogen or a C₁-C₈ hydrocarbyl substituent;
 wherein the film has an external electric field-induced
 5 net dipolar orientation of polymer molecules, and the
 film exhibits piezoelectric properties.

6. An electret film in accordance with claim 5
 wherein R in the copolymer formula is hydrogen or methyl,
 and R¹ is methyl.

10 7. An electret film in accordance with claim 5
 wherein the film is characterized additionally by a
 crystallographic orientation of copolymer molecules in
 the film plane which has been induced by mechanical
 stretching.

15 8. An electro-acoustic conversion or electro-
 mechanic conversion or pressure-sensitive device having
 an electret film component of a copolymer which is
 characterized by alternating monomeric units
 corresponding to the formula:

20



14

where R is hydrogen, halogen of a C₁-C₄ alkyl substituent;
and R¹ is hydrogen or a C₁-C₈ hydrocarbyl substituent;
wherein the film has an external electric field-induced
net dipolar orientation of polymer molecules, and the
5 film exhibits piezoelectric properties.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US90/06751

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC (5): C08F 222/34; B29C 35/02; B06B 1/02; G11C 13/02 U.S. CL. 526/300; 264/22, 24; 307/400																													
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; border-bottom: 1px solid black;">Classification System</th> <th style="border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="border: 1px solid black; text-align: center; padding: 5px;">U.S.</td> <td style="border: 1px solid black; padding: 5px;">526/300; 307/400; 264/22, 24</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	U.S.	526/300; 307/400; 264/22, 24																							
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III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border-bottom: 1px solid black;">Category [*]</th> <th style="border-bottom: 1px solid black;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 15%; border-bottom: 1px solid black;">Relevant to Claim No. ¹³</th> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">US, A, 4,591,465 (MIYATA ET AL) 27 MAY 1986 See the entire document.</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-8</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">US, A, 2,975,158 (SAYRE) 14 MARCH 1961 See the entire document.</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-8</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">US, A, 2,716,106 (GILBERT ET AL) 23 AUGUST 1955; See the entire document.</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-8</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">US, A, 4,302,408 (ICHIHARA ET AL) 24 NOVEMBER 1981; See the entire document.</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-8</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">US, A, 4,767,169 (TENG ET AL) 30 AUGUST 1988 See the entire document.</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-8</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">US, A, 2,615,868 (MILLER) 28 OCTOBER 1952 See the entire document.</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-8</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">US, A, 2,716,105 (GILBERT ET AL) 23 AUGUST 1955; See the entire document.</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-8</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">US, A, 4,684,337 (BAUER) 04 AUGUST 1987 See the entire document.</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-8</td> </tr> </table> <div style="margin-top: 10px;"> <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>[*] Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Δ" document member of the same patent family</p> </div> </div> </div>			Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	A	US, A, 4,591,465 (MIYATA ET AL) 27 MAY 1986 See the entire document.	1-8	A	US, A, 2,975,158 (SAYRE) 14 MARCH 1961 See the entire document.	1-8	A	US, A, 2,716,106 (GILBERT ET AL) 23 AUGUST 1955; See the entire document.	1-8	A	US, A, 4,302,408 (ICHIHARA ET AL) 24 NOVEMBER 1981; See the entire document.	1-8	A	US, A, 4,767,169 (TENG ET AL) 30 AUGUST 1988 See the entire document.	1-8	A	US, A, 2,615,868 (MILLER) 28 OCTOBER 1952 See the entire document.	1-8	A	US, A, 2,716,105 (GILBERT ET AL) 23 AUGUST 1955; See the entire document.	1-8	A	US, A, 4,684,337 (BAUER) 04 AUGUST 1987 See the entire document.	1-8
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IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;">Date of the Actual Completion of the International Search</td> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;">Date of Mailing of this International Search Report</td> </tr> <tr> <td style="text-align: center; padding: 5px;">20 MAY 1991</td> <td style="text-align: center; padding: 5px;">21 JUN 1991</td> </tr> <tr> <td style="border-bottom: 1px solid black; padding: 5px;">International Searching Authority</td> <td style="border-bottom: 1px solid black; padding: 5px;">Signature of Authorized Officer</td> </tr> <tr> <td style="text-align: center; padding: 5px;">ISA/US</td> <td style="text-align: center; padding: 5px;">for Nabil Sarofim</td> </tr> </table>			Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	20 MAY 1991	21 JUN 1991	International Searching Authority	Signature of Authorized Officer	ISA/US	for Nabil Sarofim																			
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	US, A, 4,830,795 (SCHEINBEIM ET AL) 16 MAY 1989; See the entire document.	1-8
A	US, A, 4,346,505 (LEMONON ET AL) 31 AUGUST 1982; See the entire document.	1-8
A	US, A, 4,435,359 (MICHERON) 24 AUGUST 1982 See the entire document.	1-8
A	SU, A, 887574 (MOSCOW LEMONOSOV UNIV) 07 DECEMBER 1981; See entire Derwent Abstract.	1-8
A	JP, A, 60-94414 (MITSUI TOATSU CHEM INC) 27 MAY 1985; See entire Derwent Abstract.	1-8
A	US, A, 4,668,449 (SONI ET AL) 26 MAY 1987 See the entire document.	1-8
A	US, A, 4,863,648 (SCHEINBEIM ET AL) 05 SEPTEMBER 1989; See the entire document.	1-8
A	DE, B, 1 137 553 (FARBWERKE HOECHST) 04 OCTOBER 1962; See entire Derwent Abstract.	1-8
A	GB, A, 756,839 (B.F. GOODRICH) 12 SEPTEMBER 1956; See the entire document.	1-8
A	JP, A, 1-103614 (MITSUBISHI PETROCH KK) 20 APRIL 1989; See entire Derwent Abstract.	1-8
A	EP, A, 0 264 240 (MITSUBISHI PETROCH KK) 20 APRIL 1988; See the entire document.	1-8
A, E	US, A, 4,990,584 (KISHIMOTO ET AL) 05 FEBRUARY 1991; See the entire document.	1-8